On the Superlattice of Binary Alloys with a Large Unit Cell and of Many-Component Alloys. I : On the Superlattice of Binary Alloys with a Large Unit Cell

On the Superlattice of Binary Alloys with a Large Unit Cell and of Many-Component Alloys. I
On the Superlattice of Binary Alloys with a Large Unit Cell*

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Synopsis

Characteristic behaviours which would appear during the formation of a binary superlattice with a large unit cell were systematically discussed first by dividing the crystal lattice into many equivalent sublattices and then by assorting them according to their mutual distances of respective lattice points, using the formal theory usually adopted. By this procedure, the classification and the nomenclature of types of superlattice were undertaken. To describe a superlattice with a large unit cell, long range interactions among atoms must be taken into account at least formally according to the type of crystal lattice and the unit cell to be considered, and the usual treatment with the nearest neighbour interaction fails to represent the characteristic natures of such a superlattice. According to the necessary range of interaction energy which should be taken into account in describing the superlattice concerned, we calssified the superlattices in a binary system into those of *first order, second order* and so on. According to the formal theory, a superlattice of a higher order corresponds to a lower temperature phase, and this makes transitions successively to stages of lower order and to the completely disordered state with the rise of temperature, though there may also be a case in which a direct transition to the completely disordered state occurs. In view of the short range nature of the interaction among atoms in metals, the formation of higher order superlattice, practically higher than the second order one, will be frozen in a lower order stage and not be realized, if the ordering energy is solely composed of the interaction energy between the pairs of atoms as is the case with the formal theory. The stabilization of such a superlattice with a large unit cell must be due rather to the lowering of the kinetic energy of electrons by the splitting of Brillouin zones corresponding to the ordering of atoms.

I. Introduction

Generally the theory of superlattice formation is treated with the nearest neighbour assumption and qualitatively well coincides with experiments. As there are some uncertainties as to whether or not the energy of superlattice formation can be expressed by the total sum of such interaction energies of definite magnitude between each pair of atoms,[1] it will be necessary to consider to what extent such a formal theory can explain the general characteristics of superlattice, because the difference between the above results and the actual properties suggests what sort of consideration we must take into account about the ordering energy in a particular case.

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* The 658th report of the Research Institute for Iron, Steel and Other Metals.

(1) H. Sato, Sci. Rep. RITU A 1 (1949), 405.

In forming a superlattice in a metallic solid solution, a necessary condition for the transition from a disordered state to an ordered state is that the change in the interaction energies between each pair of atoms due to the change in the degree of order is small.(1) Accordingly, such a transformation preferentially occurs in especially highly symmetric crystal lattices; in fact nearly all representative superlattices are found in b.c.c., f.c.c. and h.c.p. lattices, which will be an indirect justification of this requirement.

A crystal lattice with a high degree of symmetry may be divided into many equivalent sublattices. A b.c.c. lattice, for example, is divided into two equivalent s.c. lattices, four f.c.c. lattices, 16 s.c. lattices, etc.. According to the way in which different kinds of atoms occupy these sublatticepoints, the type of superlattice may be determined. For example, in a b.c.c. structure, a superlattice of the type A_3B, will be established when three of the four f.c.c. sublattices are occupied by A atoms, the remaining one being occupied by B atoms, and in the case of the type A_5B_3, the lattice must be divided into 16 s.c. sublattices and A atoms are allotted to 10 of these and B atoms to the remaining ones. The same is true also of a many-component system. For example, in a ternary superlattice of the type A_2BC in b.c.c. lattice as Heusler alloy, Cu_2MnAl, two of the four f.c.c. sublattices are occupied by A atoms and the remaining two sublattices are occupied by B and C atoms, respectively. Though the division of a lattice into sublattices is always possible in the case of a high degree of crystal symmetry, it is questionable if the sort of superlattice to be treated changes with such an artificial mode of division of lattice, or if we may always discuss the superlattice with a large unit cell if we divide a crystal lattice into a necessary number of sublattices.

Our object is, therefore, first to solve the above problem according to the geometrical nature of crystal lattice from the point of view of the formal theory and second to give a general basis for the classification and the nomenclature of superlattice by utilizing these general characteristics. Chapters II~V treat the superlattice of binary system from this point of view.

The results thus obtained did not necessarily agree with the actual properties of alloys. This might be due to somewhat incorrect assumptions on the ordering energy and so some simple considerations about the possible origin of the stabilization of a superlattice with a large unit cell are given in chapter VI.

II. Division of a crystal lattice into sublattices and their classification

Divide a crystal lattice into a sufficiently large number of sublattices and let the number be n. Such a division can be made at will according to the type of the crystal lattice. But, if we attend to one sublattice and take the shortest distance between the lattice point in it and that in other sublattice as a measure, they are assorted into several groups according to the distance.

1. Nearest neighbouring sublattice group

Take out one of sublattices and divide the whole number of sublattices into two groups, the one to which this sublattice and those at its nearest neighbouring

distance belong and the other to which the remaining sublattices belong. If the same process is carried out in each group, it will further be divided into two groups each. By the succession of this process, a lattice will finally be divided into equivalent *nearest neighbouring sublattice groups*, each of which contains the same number of sublattices. Each sublattice belonging to a different group is at the nearest neighbouring atomic distance, but in the same group each sublattice is at a larger distance than that of the nearest neighbour. Let the number of these groups be P_1, then each group contains n/P_1 of original sublattices.

2. Second nearest neighbouring sublattice group

If a similar process to the above is carried out in one of the nearest neighbouring sublattice groups, taking the second nearest atomic distance as a measure, this group can be divided into mutually equivalent sublattice groups, Q_2 in number, quite similarly as above. As each nearest neighbouring sublattice group is equivalent to each other, they are similarly divided into Q_2 *second nearest neighbouring sublattice groups* respectively. The number of mutually equivalent second nearest neighbouring groups is P_1Q_2 in all and each group contains n/P_1Q_2 of original sublattices.

By continuing a similar process further, we can classify the whole sublattices into successive groups according to the interatomic distance between each group taken as a measure. It is a noticeable fact that each group is always derived

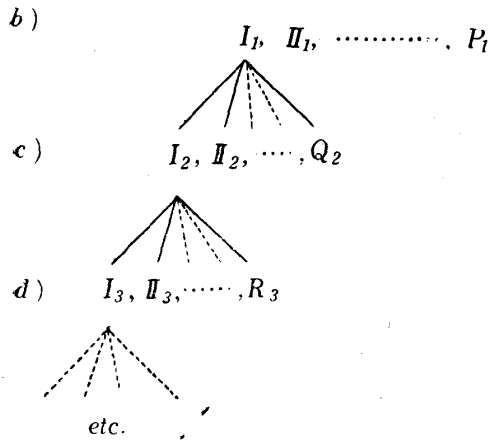

Fig. 1. Schematic representation of the mode of the division of n sublattices into successive groups. Each nearest neighbouring group contains n/P_1 original sublattices and each second nearest neighbouring group contains $n/P_1 \cdot Q_2$ original sublattices and so on.

b stage: Nearest neighbouring groups.

c stage: Second nearest neighbouring groups.

d stage: Third nearest neighbouring groups.

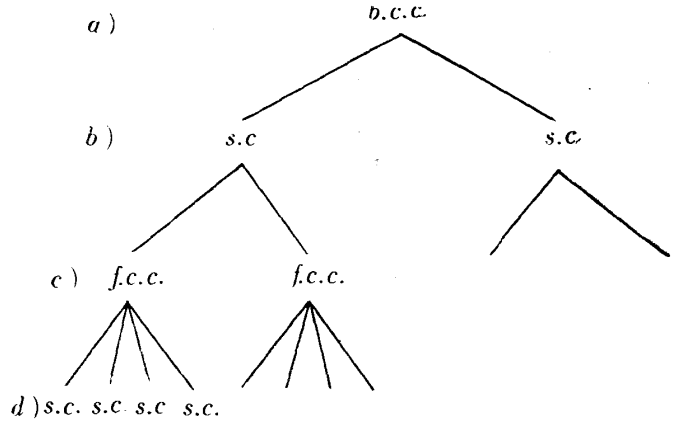

Fig. 2. The mode of the division of original lattice into successive sublattice groups in the case of b.c.c. crystals.

i) a stage: Original lattice. Lattice spacing is c.

ii) b stage: Nearest neighbouring groups. They form two interpenetrated simple cubic lattices, lattice spacing being a.

iii) c stage: Second nearest neighbouring groups. Four interpenetrated face centered cubic lattices, lattice spacing being $2a$.

iv) d stage: Third nearest neighbouring groups. 16 interpenetrated simple cubic lattices, lattice spacing being $2a$.

successively from the group, the measure at the division of which is the inter-lattice point of the one step smaller distance than the former as shown in Fig. 1.

Let us take a b.c.c. lattice for an example. In this crystal lattice the number of the nearest neighbouring group is two and each group constitutes a simple cubic sublattice as a whole. This is equivalent to the fact that a b.c.c. lattice can be divided into two interpenetrated simple cubic sublattices. Each of these sublattice groups is further divided into two second nearest neighbouring groups and each of these constitutes a f.c.c. sublattice. The third nearest neighbouring sublattice groups correspond to 16 s.c. sublattices, each four of which are derived from one second nearest neighbouring sublattice group and so on. This relation is represented in Fig. 2 as a special case of Fig. 1.

III. Energy representation of the system and the definition of the order of superlattice type

The energy of the system regarding the atomic configuration is given formally by the sum of interaction energies between all pairs of atoms. Other conceivable energy terms relating to the ordering of atoms are here neglected. Let the interaction energies between nearest neighbouring atoms, second nearest neighbours, etc. be E_1, E_2, etc., respectively, then the energy of the system will be given by

$$E=\sum_{\mu_1\leqq\nu_1} E_1(\mu_1,\nu_1)+\sum_{\mu_2\leqq\nu_2} E_2(\mu_2,\nu_2)+\cdots\cdots \qquad (1)$$

Here μ_1, ν_1, etc., denote different groups of nearest neighbouring sublattice and $E_1(\mu_1,\nu_1)$ denote the sum of the interaction energies between the nearest neighbouring atomic pairs on the respective sublattice groups. μ_2, ν_2, etc. and $E_2(\mu_2,\nu_2)$, etc. are the similar symbols for the second nearest neighbouring groups. If we further consider the circumstance that each sublattice group is derived from the preceding sublattice group as above shown, (1) will be rewritten as

$$E=\sum_{\mu_1\leqq\nu_1} E_1(\mu_1,\nu_1)+\sum_{\mu_1}\sum_{\mu_{2\mu_1}\leqq\nu_{2\mu_1}} E_2(\mu_{2\mu_1},\nu_{2\mu_1})+\sum_{\mu_1}\sum_{\mu_{2\mu_1}}\sum_{\mu_{3\mu_2\mu_1}\leqq\nu_{3\mu_2\mu_1}} E_3(\mu_{3\mu_2\mu_1},\nu_{3\mu_2\mu_1})+\cdots\cdots, \qquad (2)$$

in which $\mu_{2\mu_1}$ means the μ_2 second nearest neighbouring sublattice group belonging to the μ_1 nearest neighbouring sublattice group and the same applies to others alike. It is to be noted here that the energy of the whole system can be classified in terms corresponding to each sublattice group.

Now we limit the range of the interaction energy only to the nearest neighbouring distance for the time being as done in the ordinary treatment. As seen from (2), only the first term is considered. This means that it is sufficient to divide the crystal lattice only into the first neighbouring sublattice groups as far as the energy term is concerned. The number of equivalent sublattices to be considered is then P_1. Now we take a superlattice, say A_xB_y, and let the minimum number of sublattices necessary to describe this be m. Let a_1 be any integral number and if

$$P_1=a_1m \qquad (3)$$

holds, the treatment of such a type of superlattice is possible with this energy range. Although $P_1<a_1m$, yet the description of this type seems to be possible by dividing the crystal lattice into a larger number of sublattices. However large the number of divided sublattices may be, there will be no interaction between such sublattices that are not the nearest neighbouring to one another and as far as there is no interaction, the arrangement of atoms among such sublattices is unquestionablly disordered, because, in this case, the state is determined solely by the entropy term which is the largest in the disordered arrangement. At any rate, when the relation $P_1=a_1m$ holds, we call the superlattice A_xB_y the first order superlattice. Next, when the relation (3) does not hold, but

$$P_1Q_2=a_2m\,, \qquad (4)$$

we call this as the *second order superlattice*. In this case, it is necessary to take into account at least the second neighbour interaction for its treatment as easily seen. If we further define the superlattice with a large unit cell similarly as the above, we can classify the superlattice in a binary system from the relation that into what degree of sublattice group we must divide the original lattice for the description of the superlattice concerned; in other words, the superlattice can be classified according to the necessary range of interaction energy.(2) We will again take a b.c.c. lattice for an example. From the above definition, the superlattice in this crystal lattice can be classified according to the composition formula as follows:

the first order superlattice	AB,
the second 〃 〃	A_3B, AB_3,
the third 〃 〃	$A_{15}B$, A_7B, $A_{13}B_3$, $A_{11}B_5$, A_5B_3, A_9B_7, ····· .

The above definition can be extended to the case not completely stoichiometric. There are also some varieties according to the mode of arrangement and even though it seems to be a superlattice of lower order from the composition formula, there may be cases of higher order. The type AB, for example, may be a second order superlattice. This case is represented in Fig. 3. Thus, by describing the composition formula and the order of the superlattice type, we can give the nomenclature of a

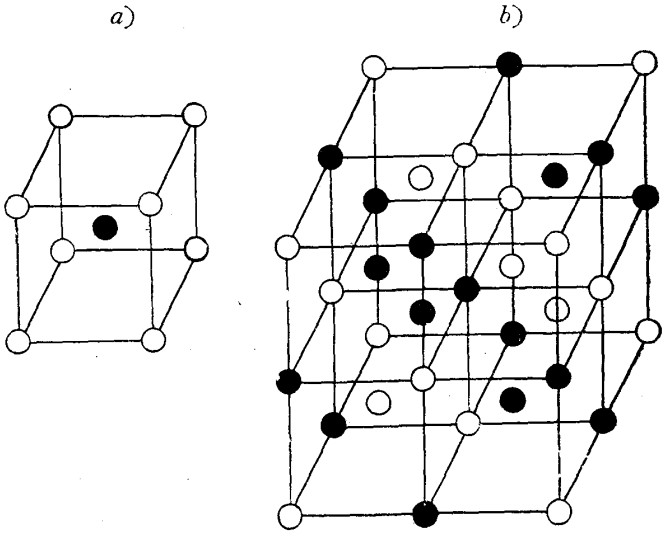

Fig. 3. Graphical representation of the arrangement of atoms in the AB type first order or second order superlattice of b.c.c. lattice.
a) AB type first order superlattice.
b) AB type second order superlattice.

(2) H. Sato, Sci. Rep. RITU **A 3** (1951), 24.

superlattice in binary system from the unified standpoint, from which we can also understand its general characteristics.

IV. Qualitative discussions about the general characteristics

In order to describe the general characteristics of a higher order superlattice, let us consider the free energy of the system. For brevity, we first adopt Bragg-Williams' approximation for its calculation, which seems to be sufficient for the qualitative description of the general characteristics.

1. Additivity of the internal energy E

From (2), the internal energy is given by the respective sum of the energy terms corresponding to sublattice groups of each order. Thus, the energy depends on the relative distribution of atoms on each equivalent sublattice group of respective orders but not on the arrangement on the particular sublattice.

2. Entropy

Let the entropy corresponding to the superlattice with the nth order sublattices be Φ_n. If we divide a crystal lattice into the nth order sublattices, the entropy of the system Φ will be equal to Φ_n. Hence,

$$\Phi = \Phi_1 + (\Phi_2 - \Phi_1) + (\Phi_3 - \Phi_2) + \cdots\cdots + (\Phi_n - \Phi_{n-1}) \qquad (5)$$

Φ_1 corresponds to the entropy of the system in which the atoms on each sublattice group of the first order are distributed at random as far as the number of atoms of each sort on each sublattice is fixed. This is equal to the entropy of the first order superlattice in B-W approximation. Φ_2, Φ_3, etc. represent those of sublattices of the second order, third order, etc., respectively. In B-W approximation, however, the interdependence between each group is neglected and the degree of approximation falls with the fineness of the division of the original lattice into sublattices. Nevertheless we take it tolerable, because in practice we are forced to give up the treatment about the superlattice presumably higher than the second order, owing to the probable smallness of the interaction between the higher order sublattices.

From (2) and (5), the free energy may be written as

$$F = \{ \sum E_1(\mu_1, \nu_1) - T\Phi_1 \} + \{ \sum\sum E_2(\mu_2, \nu_2) - T(\Phi_2 - \Phi_1) \} + \cdots\cdots \qquad (6)$$

and be divided into those of sublattice groups of each order. This is the additivity of free energy. Independent of the extent of the range of energy, the entropy is evaluated according to the mode of division.

Now the meaning of the additivity of free energy will be examined below. First, only the nearest neighbour interaction is taken into account as an example, higher energy terms than E_2 being zero. Let us consider the equilibrium state of this case. Let the parameter representing the relative distribution of atoms on each nearest neighbouring sublattice group in B. W. approximation be α and that between the second nearest ones be β, etc.. In this case, we may put, from the form of (2) and (5), the functional forms of E and Φ as $E_1(\alpha)$, $E_2(\alpha, \beta)$, $E_3(\alpha, \beta, \gamma)$, ……, and $\Phi_1(\alpha)$, $\Phi_2(\alpha, \beta)$, $\Phi_3(\alpha, \beta, \gamma)$, …… respectively. The

equilibrium state will then be given by

$$\frac{\partial F}{\partial \alpha}=0; \qquad \frac{\partial F}{\partial \beta}=0; \cdots\cdots\cdots .$$

As the energy terms higher than E_2 are zero, these become

$$\frac{\partial E_1}{\partial \alpha}-T\frac{\partial \Phi_n}{\partial \alpha}=0; \quad \frac{\partial \Phi_n}{\partial \beta}=0; \cdots\cdots\cdots; \quad \frac{\partial \Phi_n}{\partial \nu}=0 \qquad (7)$$

In order to make the free energy minimum, the entropy expression Φ_n must be maximum for the parameters representing the arrangement of atoms on higher sublattices than the second order one; in other words, the arrangement is random in such sublattices, hence, Φ_n is equal at least to Φ_{n-1} which corresponds to the distribution of both atoms on the $n-1$st order sublattice. In the degree of approximation of Stirling's formula, this is reduced successively to

$$\Phi_n=\Phi_{n-1}; \quad \Phi_{n-1}=\Phi_{n-2}, \cdots\cdots\cdots, \quad \Phi_2=\Phi_1,$$

and finally to

$$\Phi_n=\Phi_1. \qquad (8)$$

The discussion of the equilibrium state may be possible only with the first formula of (7), $\frac{\partial E_1}{\partial \alpha}-T\frac{\partial \Phi_1}{\partial \alpha}=0$. This form is quite the same as that obtained by dividing the crystal lattice only into the nearest neighbouring sublattices and applying the B-W calculation to it. It will thus be clear that it is meaningless that into how many sublattices we may divide the crystal lattice for describing the superlattice with a large unit cell and that the number of sublattices to be divided depends solely upon the range of interaction taken into account.

The above conclusion holds strictly only in such a case in which the calculation of the entropy can be carried out separately on each sublattice as in B-W approximation. However, as the division of a lattice is necessary when the complete order is maintained and as the entropy in B. W. approximation is maximum so far as the divided number of sublattices is fixed, and also as the classification of energy into successive order is independent of the approximate method, the result of the above method will hold also in the more advanced method without so many alterations. Consequently, it may be concluded that when the higher order interaction must be taken into consideration, the higher order superlattice corresponding to the order of interaction may develop at lower temperatures. As the interaction between atoms in metals, however, is of short range, the energy difference between the higher order superlattice and the lower order superlattice which is of higher symmetry is considered to be small. (What is to be compared in this case, is not the magnitude of particular interaction but the difference between the interaction of pairs of similar atoms and that of different atoms. The ratio of the magnitude of interaction of higher order to that of lower order is thus not always negligible.*) By raising temperature, the higher order superlattice makes transitions successively to the lower order stages with higher

* Such consideration holds particularly in such a case in which $V_{AA}+V_{BB}-2V_{AB}\sim 0$, where V_{AA}, V_{BB} and V_{AB} are the nearest neighbour interactions, respectively.

entropy and at last to the completely disordered state. The superlattice Fe_3Al with b.c.c. lattice, for example, which is a second order superlattice, is expected, when heated, to make a transition to the completely disordered state passing through the first order superlattice of FeAl type. Actually, Fe-Al alloys containing more than 14% of Al (25 atomic percent) has been known to make a transition from Fe_3Al type to FeAl type.(3) As a peak of anomalous specific heat is to be perceived at such a transition point, it will be expected to have several peaks of anomalous specific heat from biginning to the completely disordered state, which is one of characteristics of the existence of a higher order superlattice. According as the relative magnitude of the interactions of respective orders, there may be a case in which higher order superlattice makes a transition directly to the completely disordered state. Theoretically, latent heat is ordinarily to be perceived in such a case. (The superlattice of Fe_3Al type, for example, makes a transition to the disordered state in alloys containing less than 14% of Al.(3)) The following points should also be noticed in connection with the existence of higher order superlattice under the above assumption about configurational energy. As the difference in energy between higher order superlattice and lower order one is small, the existence range of a higher order superlattice in an equilibrium state is ordinarily limited to the lower temperatures. On the other hand, as the frequency of exchanging positions of atoms becomes very small at lower temperatures and as the realization of higher order superlattice requires long range atomic ordering, the possibility is very high that the state is frozen in the lower order state. It seems to be an example for this that in Fe-Al alloys in which the Fe_3Al type of ordering is to be realized, the FeAl type but not Fe_3Al type is realized when quenched from high temperatures. This may be due to insufficient time available for the formation of the type Fe_3Al.

In a b.c.c. lattice, the existence of the second order superlattice of the above meaning plays an important role, because the ratio of the distance of the nearest neighbouring atomic pair to that of the second nearest one is small as compared with other types of lattice,(2) and, further, superlattices higher than the third order are generally considered not to be realized, being frozen in a lower order state, if the interaction energy between the pair of more distant atoms in the above sense is solely responsible for the formation of superlattice with a large unit cell. The origin of the existence of a peculiar type of superlattice must thus be sought for in other energy terms. (Cf. Chapter VI)

V. Quantitative treatment of free energy

To make the above discussions quantitative, the free energy of the system and the equilibrium state derivable from it will be calculated in simple cases by B-W approximation.

1. A case in which only the nearest neighbour interaction is taken into account.

Divide the crystal lattice into n equivalent sublattices and let the number of the

(3) A. J. Bradley and A. H. Jay, Proc. Roy. Soc., **136A** (1932), 210.

nearest neighbouring sublattice groups be P_1. Then any sublattice can be represented by the number $pm+q$, $p=0, 1, 2, \cdots\cdots, p_1-1$; $q=1, 2, 3, \cdots\cdots, m$; $m=n/p_1$. Sublattices of the same p belongs to the same nearest neighbouring sublattice group. Denote the number of A atoms on the $pm+q$th sublattice by the symbol $[A/pm+q]$. Then by defining the parameters α_{pm+q}, etc. as below, $[A/pm+q]$, etc. are given by

$$[A/pm+q] = \frac{N}{n}\,\frac{1+\alpha_{pm+q}}{2}\,. \tag{9}$$

The parameter α_{pm+q} is defined to take the value $+1$ when all points of the $pm+q$th sublattice are occupied by A atoms and -1 when none of them is occupied by A atoms. The energy of the whole system is then given by B. W. approximation by

$$\left.\begin{aligned} E =& \frac{N}{n} Z_1 \frac{1}{2} \sum_p \Big[\sum_q \frac{1+\alpha_{pm+q}}{2} \Big] \Big[\sum_{p' \neq p} \sum_{q'} \frac{1+\alpha_{p'm+q'}}{2} \Big] V_{AA} \\ &+ \frac{N}{n} Z_1 \frac{1}{2} \sum_p \Big[\sum_q \frac{1-\alpha_{pm+q}}{2} \Big] \Big[\sum_{p' \neq p} \sum_{q'} \frac{1-\alpha_{p'm+q'}}{2} \Big] V_{BB} \\ &+ \frac{N}{n} Z_1 \frac{1}{2} \sum_p \Big[\sum_q \frac{1+\alpha_{pm+q}}{2} \Big] \Big[\sum_{p' \neq p} \sum_{q'} \frac{1-\alpha_{p'm+q'}}{2} \Big] V_{AB} \\ &+ \frac{N}{n} Z_1 \frac{1}{2} \sum_p \Big[\sum_q \frac{1-\alpha_{pm+q}}{2} \Big] \Big[\sum_{p' \neq p} \sum_{q'} \frac{1+\alpha_{p'm+q'}}{2} \Big] V_{AB}\,, \end{aligned}\right\} \tag{10}$$

where Z_1 is the number of the nearest neighbouring atoms. The entropy Φ is given by

$$\Phi = -k \log W\,, \tag{11}$$

$$W = \prod_p \prod_q \frac{\left(\frac{N}{n}\right)!}{\left(\frac{N}{n}\,\frac{1+\alpha_{pm+q}}{2}\right)!\left(\frac{N}{n}\,\frac{1-\alpha_{pm+q}}{2}\right)!}\,. \tag{12}$$

The freeenergy F is then obtained by

$$F = \sum_p F_p\,, \tag{13}$$

$$\left.\begin{aligned} F_p =& \frac{N}{n} Z_1 \frac{1}{2} \Big[\sum_q \frac{1+\alpha_{pm+q}}{2} \Big] \Big[\sum_{p' \neq p} \sum_{q'} \frac{1+\alpha_{p'm+q'}}{2} \Big] V_{AA} + \cdots\cdots \\ &- kT \log \prod_q \frac{\left(\frac{N}{n}\right)!}{\left(\frac{N}{n}\,\frac{1+\alpha_{pm+q}}{2}\right)!\left(\frac{N}{n}\,\frac{1-\alpha_{pm+q}}{2}\right)!}\,. \end{aligned}\right\} \tag{14}$$

From the relation

$$\frac{N}{n} \sum_p \sum_q \frac{1+\alpha_{pm+q}}{2} = NC_A\,, \tag{15}$$

where C_A is the concentration of A atom, it follows

$$\sum_{p' \neq p} \sum_{q'} \frac{1+\alpha_{p'm+q'}}{2} = NC_A - \sum_q \frac{1+\alpha_{pm+q}}{2}\,,$$

in which $\sum_{p' \neq p} \sum_{q} \alpha_{p'm+q'}$ is replaced by $\sum_{q} \alpha_{pm+q}$. The problem to seek for n α_{pm+q}'s is reduced to that for the minimum of F_p and the number of variables can thus be reduced to $1/P_1$.

Further, α_{pm+q} can be proved to be equal to one another, irrespective of q, that is, from (10)

$$\frac{\partial E}{\partial \alpha_{pm+q}} = \frac{\partial E}{\partial \alpha_{pm+q'}} .$$

In equilibrium state, $\frac{\partial F_p}{\partial \alpha_{pm+q}} = 0$, hence,

$$\frac{\partial \Phi_p}{\partial \alpha_{pm+q}} = \frac{\partial \Phi_p}{\partial \alpha_{pm+q'}} .$$

From (14), this becomes

$$\log \frac{1+\alpha_{pm+q}}{1+\alpha_{pm+q'}} = \log \frac{1-\alpha_{pm+q}}{1-\alpha_{pm+q'}} ,$$

or

$$\alpha_{pm+q} = \alpha_{pm+q'} . \tag{16}$$

In the problem of binary alloys, the equilibrium state can thus be discussed with only one parameter, α_{pm+q}, for example, irrespective of a number of sublattices, as far as only the nearest neighbour interaction is taken into account. The conclusion obtained from (16) represents that the atomic distribution on a sublattice belonging to the same nearest neighbouring group is the same and that only the distribution of atoms on the sublattice composed of all sublattices in this group is to be considered. The number of independent sublattices to be divided is equal to the number of the nearest neighbouring sublattice groups.

In the existing range of superlattice, more than one solution of α_{pm+q} will exist which are different from the value corresponding to the disordered state, $\alpha_{pm+q} = 2C_A - 1$. By allotting these different values appropriately to the P_1 independent sublattices to make $\sum F_p$ minimum, the equilibrium atomic distribution at the specified temperature will be obtained. In b.c.c. lattice, for example, the number of possible different values of α is one. There are, therefore, only two cases; either the two sublattices has the same value $\alpha = 2C_A - 1$ (disordered state) or different values (AB type). In f.c.c. lattice, the number of different values are two and it is verified that there is no other case than that of the disordered state, AB type or of AB_3 type (or A_3B type). (The case in which two of four independent sublattices take the same value of the disordered state and the remaining two have two different values, respectively, does not correspond to the equilibrium state and is excluded.(4)) Thus, the conclusion as to the number of independent sublattices previously discussed qualitatively is now made clear.

2. A case in which the interaction between the second nearest neighbouring atoms is contained.

In this case, from the same argument, it will easily be understood that the second nearest neighbouring groups become independent of one another. As the

(4) W. Shockley, J. Chem. Phys. 6 (1938), 70.

second nearest neighbouring groups are derived from each nearest neighbouring group as explained before, any sublattice can be represented by the number $pm+kl+r$, in which p and m are respectively the same as those stated before and $q=kl+r$, $k=0, 1, 2, \cdots\cdots, Q_2-1$; $r=1, 2, \cdots\cdots, l$; $l=n/P_1 \cdot Q_2$. Any sublattice of the same k belongs to the same second nearest neighbouring sublattice group. From the same argument, F_p can be divided into the sum of Q_2 equivalent expressions, and accordingly,

$$F_p = \sum_k F_{p,k} \ , \tag{17}$$

and

$$F = \sum_{p,k} F_{p,k} \ .$$

Quite similarly,

$$\alpha_{pm+kl+r'} = \alpha_{pm+kl+r} \tag{18}$$

can be verified to hold. The distribution of atoms on each sublattice belonging to the same second nearest neighbouring sublattice group is qnite the same and the number of independent sublattices is equal to that of the second nearest neighbouring groups. The calculation of the equilibrium state can then be treated with one variable per nearest neighbouring group. By allotting appropriately the values of $\alpha_{pm+kl+r}$ obtained by the calculation to the second nearest neighbouring sublattices to make the total free energy minimum, the distribution of atoms in the equilibrium state will be determined. The number of variables is, then, equal at most to the number of the nearest neighbouring groups. Though the difference of $\alpha_{pm+kl+r}$ from α_{pm+q} is easily obtained by using the purturbation theory [2] when $V \gg W$*, tedious calculations must be carried out when W becomes considerably large. When all the values of $\alpha_{pm+kl+r}$ are the same, the second order superlattice vanishes and this state corresponds either to the first order superlattice or to the completely disordered state. The conditions for the transition between these states will easily be derived from the result of the above calculation.

The above argument is applicable also to the case in which the interaction between the more distant atoms is taken into consideration. Thus the general characteristics of the nth order superlattice will be understood in general. As to more concrete problems, the theory of the second order superlattice in b.c.c. lattice** published before[2] should be referred.

VI. Possible origin of the stabilization of superlattice with a large unit cell

So far, we have discussed the superlattice with a large unit cell by using the formal theory in terms of interaction energy of definite magnitude between pairs

* V and W represent the nearest neighbour interaction and the second nearest neighbour interaction, respectively.

** An example of superlattice problem in which the second neighbour interaction was taken into account was actually calculated recently by
S. Matsuda, J. Phys. Soc. Japan, **6** (1951), 151,
K. Adachi, Sci. Rep. Tôhoku Univ., Ser. I, **35** (1951), 30.

of atoms. Together with this assumption, interaction between more distant atoms is further necessary for the explanation of a superlattice with a large unit cell. Even if such a long distance interaction can formally be used with success, theoretical justification of this fact will be difficult. Furthermore the existence of higher order superlattice may de difficult of consideration in view of the short range nature of interaction energy. Actually, however, the existence of a superlattice with a very large unit cell such as CuAu II has been reported.(5) To such a problem, the formal theory can no longer be applicable. Hence, the possible origins of the stabilization of such a superlattice with special symmetry will be examined below.

With the development of the degree of order, some properties of the alloy will change, resulting in the lowering of ordering energy.(1) If such lowering of energy overcompensates the entropy or energy terms resisting the development of order, the superlattice of corresponding symmetry may be stabilized. Among several assumable origins of this, the lowering of kinetic energy of free electrons due to the splitting of Brillouin zones seems most probable in such an alloy as CuAu II, in which the changes of the lattice type and of other properties do not occur during the superlattice formation. As well known, the state density of electrons rises sharply near the Brillouin zone boundary, resulting in the lowering of the energy of electrons just accommodated in this zone. Such aspects have been used for the explanations of several electron compounds.(6) With the development of order, the splitting of Brillouin zones will occur, corresponding to the symmetry of ordering. If the number of electrons of the alloy is that just accommodated in such splitted zone, the lowering of energy of electrons will occur which is proportional to the square of discontinuities in energy produced. This may stabilize the superlattice of the corresponding symmetry. As the discontinuity in energy thus produced is proportional to the degree of long range order S,(7) the odrering energy due to this origin is, in its form, quite equivalent to that due to the formal theory with the nearest neighbour assumption. The existence of superlattice with complex symmetry without any other particular reasons, would possibly be stabilized because of this mechanism. Under such circumstances a higher order superlattice may not necessarily pass through a lower order stage at the decomposition.

Summary

From the standpoint of a formal theory, in which the ordering energy is composed of the total sum of interaction energy of definite magnitude between each pair of atoms, general characteristics of binary alloys were discussed. The main results were as follows:

(5) C. H. Johansson and J. O. Linde, Ann. Physik, **25** (1936), 1.
(6) G. V. Raynor, Progress in Metal Physics. I, London, (1949), 1,
L. Pauling and F. J. Ewing, Rev. Mod. Phys., **20** (1948), 112.
(7) T. Muto, Sci. Pap. IPCR, 34 (1938) 377.

(1) For the explanation of a superlattice with a large unit cell, the consideration only of the nearest neighbour interaction is insufficient and the interaction between distant atoms must be taken into account.

(2) The order of superlattice was defined by the effective range of energy, which was necessary to explain the superlattice concerned. A higher order superlattice appears in the lower temperature range than a lower order one.

(3) Higher order superlattice becomes disordered passing successively through lower order stages with the rise of temperature. (The intermediate stages may be omitted.) As a result of this, several peaks may appear in a specific heat-temperature curve.

(4) In view of the short range nature of the interaction energy between atoms, the probability that the formation of a higher order superlattice is frozen in a lower order stage would be high even under the condition in which it is energitically favourable.

Utilizing these properties, the classification and the nomenclature of superlattice were undertaken. The above results also suggest that considerable cares must be taken in making a conclusion as to the existence of a higher order superlattice.

The properties of actual superlattice with a large unit cell are not always coincident with the above conclusions. This fact suggests that the assumptions about the ordering energy are not correct. Of the origins to be taken into account, the stabilization due to the lowering of kinetic energy of free electrons by the splitting of Brillouin zones was taken as most probable.

The above arguments are formally applicable also to the treatment of antiferromagnetism with Ising's model.